Pulse cathodo- and thermoluminescence of alumina ceramic with manganese

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Pulse cathodo- and thermoluminescence of alumina ceramic with manganese

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Abstract. Alumina ceramics with manganese in concentration range 0.001-18 wt. % are synthesized. Luminescent properties of obtained ceramics at temperatures 1500-1700°C of sintering in vacuum are investigated. An increase in the manganese concentration leads to quenching of the pulse cathodoluminescence band at 420 nm and the main dosimetric peak at 460 K. The intensity of luminescence in the 676 nm band at manganese concentrations of more than 1 wt. % and the TL yield for all the observed peaks increase when annealing temperature rises. Sublinear increase in TL intensity with a growing dose is observed in the range of 3-1000 Gy in 460 and 620 K peaks.

1. Introduction

The investigation of luminescent characteristics of materials is important for the creation of effective optoelectronic devices and systems. An experimental study of the optical properties of materials is of considerable interest for understanding the structural state features and predicting the properties of new functional materials. The study of charge transfer processes in wide-gap dielectrics is an actual problem in condensed matter physics, since these processes determine many of the radiation-optical, luminescent, and electrical properties of materials. Such materials can be created by forming impurity luminescence centers in their structure [1-4].

The introduction of various dopants into the original matrix of the material also leads to a significant change in the luminescent properties of the material, and, accordingly, changes in luminescence characteristics, which will be determined by the concentration of dopant in the volume of the original matrix. Oxide systems with various dopants currently have promising applications in the form of ceramics. Ceramic structures have a higher mechanical strength and stability properties. In addition, from ceramics it is possible to make samples with the necessary shape and size. The optical properties of various oxides doped with various impurities as matrices with high quantum yield of luminescence have been intensively studied. The doping leads to the new luminescence centers formation because of changes in the crystal lattice and the creation of a defective structure in the material. Among the methods of aluminum oxide doping, sol-gel method [5], powder mixing [6], hydrothermal treatment [7] and crystal growing on the plate [8] are widely used. Impregnation in a solution containing the necessary admixture [9, 10] is one of the most effective methods of impurity

introduction into compacts made of nanopowder. This method enables to vary the dopant content by changing the time and number of impregnation cycles, as well as the concentration of the solution.

2. Materials and methods

Ceramics were manufactured in multistage synthesis. Porous matrices were produced by cold static pressing under pressure 0.7 GPa from high purity (99.5 %) commercial nanopowder α-Al_2O_3 with the particle size of 20–150 nm. The compacts were discs with 10±0.05 mm in diameter and 1±0.2 mm in thickness. Before doping the compacts were tempered at 450°C for 2 hours. To obtain the impure ceramics the porous matrices was impregnated in the solutions of manganese nitrate of different concentration of Mn (0.001 wt. % and 18 wt. % in solution) for 30 min. The ceramics with impurity luminescent centers was sintered at temperature in range 1500-1700ºC and duration 2 hours in a vacuum (0.013 Pa) using high-temperature vacuum electric furnace SNVE 9/18. Part of samples was sintered in the presence of carbon, using high-purity graphite rods (20 g). Carbon is a good reducing medium and promote to producing oxygen-deficient ceramics.

Pulse cathodoluminescence (PCL) was measured by spectrometer "KLAVI" in the spectral region 300-700 nm at excitation of an electron beam with the pulse duration of 2 ns, the average energy of electron 130±10 keV, current density of 60 A/cm^2. Termoluminescence (TL) measurements were performed by the dosimetry system "Grey" using the standard method from 300 to 670 K in linear heating mode with the rate of 2 K/s by photomultiplier HAMAMATSU Photonics (Japan) 10722 H. Part of the TL experiments was performed with a narrow-band filter 420 nm to measure the glow of the internal F-centers of the alumina ceramic under study. The electron-beam gun with dose 1.5 kGy per one pulse and $^{90}Y/^{90}Sr$ β-source with a dose rate of 52 mGy/min was used to excite TL in ceramic samples.

3. Results and discussion

The PCL spectra (figures 1a,b) show that multistage synthesis leads to the formation of luminescent centers in alumina ceramics: intrinsic centers of Al_2O_3 in the 420 nm band, doped centers Mn in the 676 nm band and impurity centers present in the initial powder with small concentrations – Cr (λ=693 nm). Unidentifiable, according to the literature, the band in the 420 nm can be associated with the oxygen vacancies in alumina (F-centers – when trap two electrons complex) [11] and with aggregate centers as intrinsic defects obtained as a result of annealing in the presence of carbon and impurity centers [12]. It was determined that the increase in the annealing temperature of ceramics with low impurity concentrations (0.001-0.1 wt. %) leads to a decrease in the luminescence intensity in the 676 nm (Mn) band. In this case the luminescence intensity of the chromium band (693 nm) is dominated by it of manganese band (676 nm).

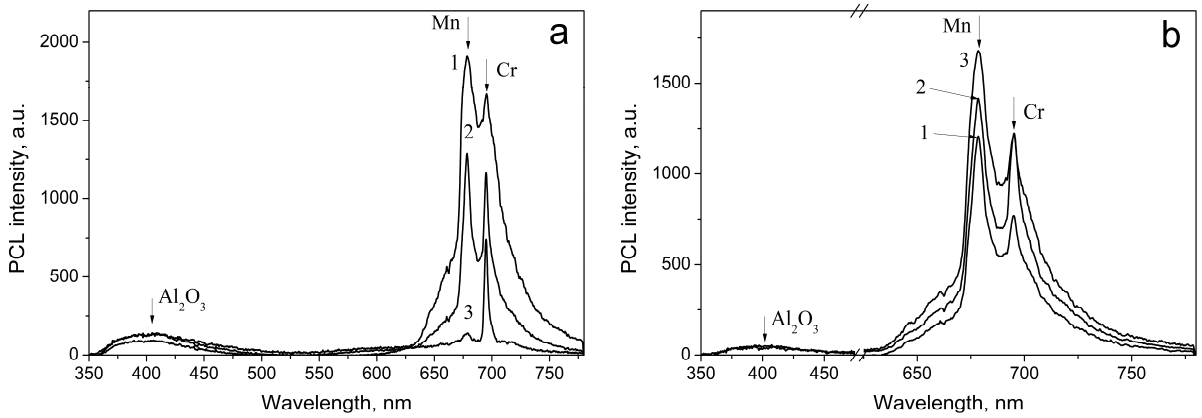

Figure 1. PCL spectra of alumina ceramics with manganese 0.1 wt. % (a) and 10 wt. %; (b) synthesized for 2 hours at different temperatures: 1 – 1500°C, 2 – 1600°C, 3 – 1700°C.

The opposite effect is observed at high manganese concentrations (more than 1 wt. %) because a rise in temperature leads to an increase in the luminescence intensity in the dopant band (676 nm). This result may be due to the fact that both impurity centers and a large number of intrinsic defects are formed as the annealing temperature of the ceramic increases. Such defects are associated primarily with oxygen vacancies. A close to a twofold increase in the PCL intensity in the 420 nm band is observed with growth of the annealing temperature for all samples at any concentration of the dopant under study. This could be the reason of luminescence quenching in the impurity center at low dopant concentrations.

This assumption is confirmed by the analysis data of the PCL spectra of alumina ceramics with varied the manganese impurity concentration in a wide range (figure 2). An increase in the dopant concentration leads to an increase in the luminescence intensity in the 676 nm band. It should be noted that there is a saturation of the luminescence in this band at a manganese concentration of 1 wt. %. However, a decrease in the luminescence intensity of the intrinsic centers of aluminum oxide (420 nm) occurs continuously with a change in the dopant concentration. This fact is primarily due to the luminescence quenching by an impurity of manganese. A constant decrease in the luminescence intensity in the 420 nm band indicates a much higher concentration of intrinsic defects of aluminum oxide compared with impurity centers.

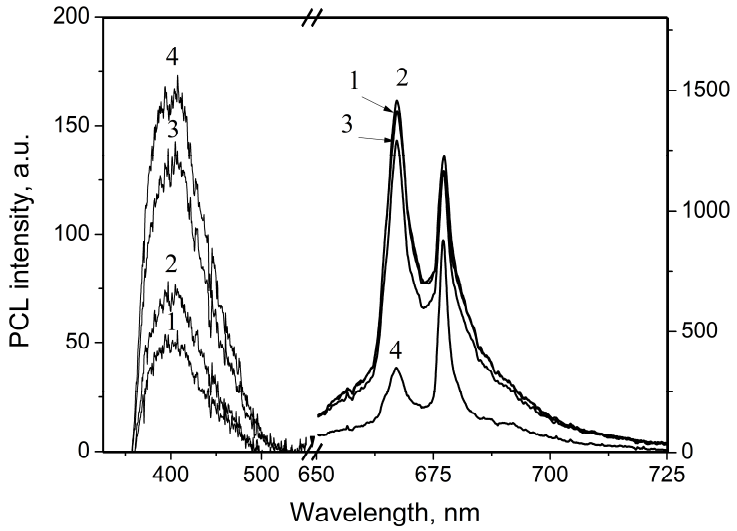

Figure 2. PCL spectra of alumina ceramics sintered at temperature 1600 °C and duration 2 hour at varying concentration of manganese: 1 – 10 wt. %, 2 – 1 wt. %, 3 – 0.1 wt. %, 4 – 0.01 wt. %.

Figure 3 shows that the presence or absence of carbon at high-temperature annealing are influenced on the luminescent properties of alumina ceramics (temperature 1600°C and duration 2 hours) with different dopant concentration. Thus, sintering in the presence of carbon at a manganese impurity concentration of 0.2 wt. % (curve 1) leads to an increase in luminescence intensity in all bands: 420, 676 and 693 nm. The creation of strongly reducing medium during high-temperature annealing due to the presence of carbon forms a more defective structure of alumina ceramics. But a decrease in the luminescence intensity of the inner center of aluminum oxide sintered in the presence of carbon is observed at concentrations of manganese close to the maximum for this method of doping It should be noted that luminescence bands is shifted to the region of lower waves at annealing with carbon. Unidentifiable, according to the literature, the band in the 420 nm can be associated with complex aggregate centers as intrinsic defects obtained as a result of annealing in the presence of carbon and impurity centers. In this connection, it can be assumed that carbon promotes the formation of new defects in ceramics, including cluster defects. Such defects interact more with impurity centers.

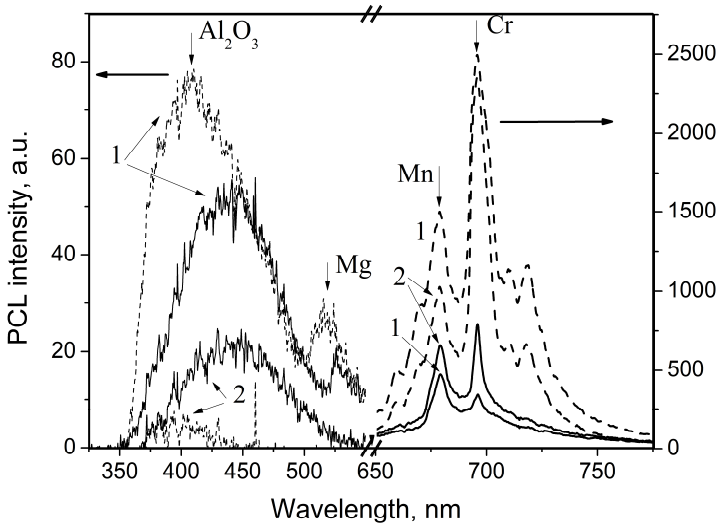

Figure 3. PCL spectra of alumina ceramics with manganese 0.2 wt. % (1) and 18 wt. % (2) exposed by electron beam irradiation with the doses 30 kGy. Solid line is curve of ceramic sintered without carbon and dash line – in presence of carbon.

For a complex analysis of luminescent properties TL measurements were made after various types irradiation of alumina ceramics with manganese. Figure 4 shows the TL curves of Al_2O_3:Mn ceramics with a dopant concentration of 0.2 and 18 wt. % sintered at a temperature of 1600°C for two hours in the presence and absence of carbon. The samples were previously irradiated with 20 electron pulses (an irradiation dose – 1.5 keV per pulse). The TL measurements in this case were performed in the presence of a narrow-band filter with a transmission wavelength of 420±10 nm. It is shown that there are three luminescence peaks with maxima at 380, 440 and 580 K in the samples with a low concentration of manganese impurity. Similar peaks correspond to the peaks of TL curves in the pure alumina ceramics [13]. Sintering in the presence of carbon leads to a decrease in the low-temperature peaks and promotes the growth of a high-temperature peak. The low-temperature peaks are mainly associated with either internal centers of luminescence in alumina (F- and F+-centers) or aggregate centers. A high-temperature peak is associated with impurity of chromium. It should be noted that these results are related to single crystal based on aluminum oxide. However, in the presence of a narrow-band filter the F-centers make the main contribution to the luminescence of the alumina ceramic with the manganese at the temperatures indicated above. Our previous studies show that the high-temperature peak has a more complex structural state in the ceramics and also experiences the influence of various impurities. The presence of a manganese impurity in high concentrations leads to a significant decrease in luminescence in all three peaks of the TL curves. This fact can be associated with quenching of luminescence by an impurity of manganese.

Figure 5 shows the TL curves of Al_2O_3:Mn ceramics with a dopant concentration of 0.001 and 18 wt. % sintered in vacuum at different temperatures. TL curves are measured in the full spectral range of the photomultiplier registration without the use of transmission filters. In this case the maxima of the luminescence peaks shift toward higher temperatures and peaks at 390, 460, and 620 K are detected. The shift of luminescence peak maxima to the high-temperature region is due to both F-centers and the complex aggregate center. It is caused by impurity centers of manganese and possibly chromium. In contrast PCL spectra, an increase in the annealing temperature of ceramics at all concentrations of manganese leads to an increase in the luminescence intensity for all peaks of the above. The annealing at a temperature of 1700°C for 2 hours provides a significant increase in luminescence intensity in comparison with annealing at a temperature of 1600°C. It should be noted that the luminescence peak with a maximum of 460 K on predominates in contrast data of figure 4. It

could be due to the fact that the measurements in this case is performed in all the spectrum of the photomultiplier registration without the presence of filters. In this connection, it can be concluded that a manganese impurity with luminescence in the 676 nm band makes the greatest contribution to the luminescence of 460 K peak. Chromium impurity found at the analysis of the PCL spectra above also can be influent on luminescence intensity of 460 K peak. The concentration quenching begins to appear at high concentrations of manganese impurity (figure 5b) in ceramics sintered at temperature of 1700°C. It leads to approximately the same luminescence intensity of peaks with maxima at 380 and 460 K.

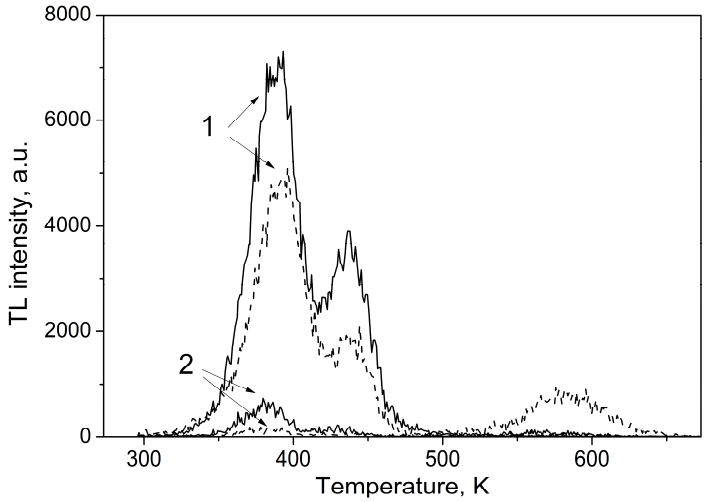

Figure 4. TL curves of alumina ceramics with manganese 0.2 wt. % (1) and 18 wt. % (2) exposed by electron beam irradiation with the doses 30 kGy. Solid line is curve of ceramic sintered without carbon and dash line – in presence of carbon.

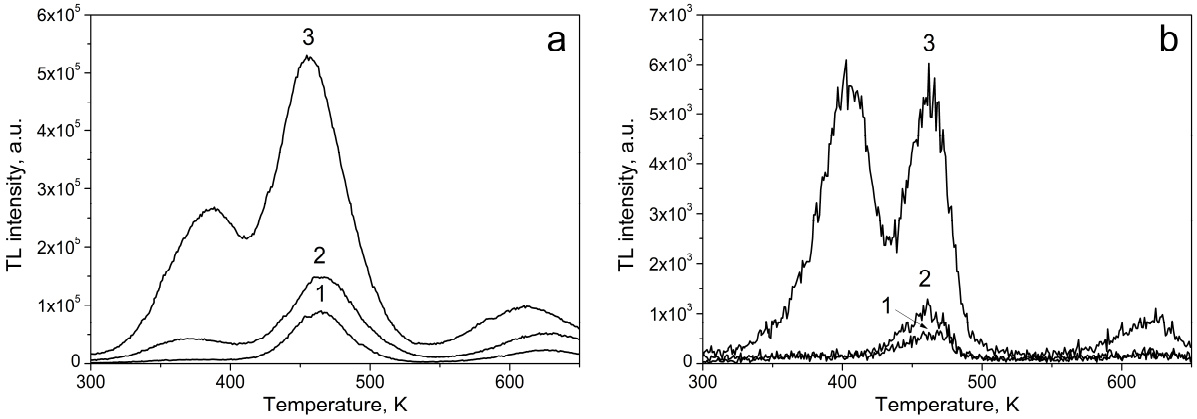

Figure 5. TL curves of alumina ceramics with manganese 0.001 wt. % (a) and 18 wt. % (b) under electron beam irradiation with the doses 30 kGy synthesized for 2 hours at different temperatures: 1 – 1500°C, 2 – 1600°C, 3 – 1700°C.

The effect of the manganese concentration on the TL can be estimated on the basis of the data presented in figure 6. It shows the TL curves of alumina ceramics sintered at a temperature of 1600°C for 2 hours with a manganese concentration in range 0.001-18 wt. %. It was seen that an increase in the impurity concentration leads to a decrease in the TL yield for all the measured peaks. This may be

due to both the concentration quenching of manganese luminescence and the quenching of the luminescence of the F- and F+-centers by impurities. This may also be related to competing processes between the impurity, internal, aggregate and may be cluster centers.

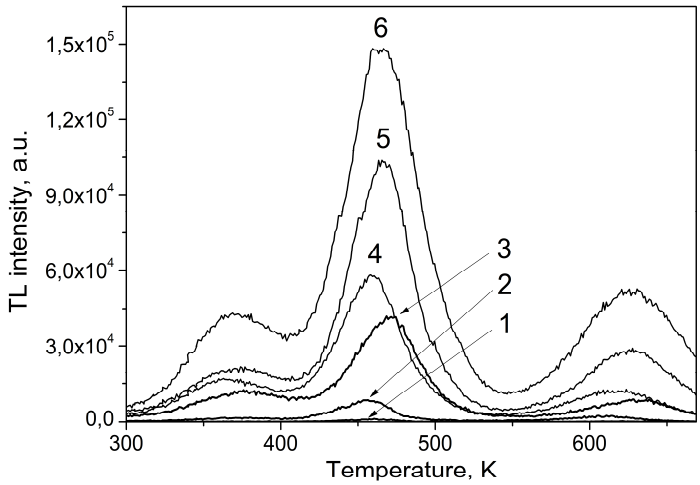

Figure 6. TL curves of alumina ceramics sintered at temperature 1600 °C and duration 2 hour at varying concentration of manganese: 1 – 18 wt. %, 2 – 10 wt. %, 3 – 1 wt. %, 4 – 0.1 wt. %, 5 – 0.01 wt. %, 6 – 0.001 wt. %.

To analyze the sensitivity to radiation dose a sample sintered at a temperature of 1500°C for 2 hours with a manganese concentration of 1 wt. % was chosen. It had the largest ratio between the PCL intensity of the impurity center of manganese and chromium. It was shown that this sample is sensitive to the dose of $^{90}Y/^{90}Sr$-source β-radiation (figure 7). Thus, the intensity of TL in the peaks of 460 and 620 K is observed. It should be noted that the low-temperature peak of 380 K is absent in the measured dose range (1-1000 Gy) for $^{90}Y/^{90}Sr$-source β-radiation in contrast to TL curves after the irradiation with a pulse electron beam. The pure ceramics of alumina are sensitive to this kind of radiation even at 0.03 Gy [14]. The TL can be registered only at dose more than 1 Gy for ceramics of Al_2O_3:Mn. This fact can contribute to a shift in the linear range of detection of ionizing radiations to higher values of dose.

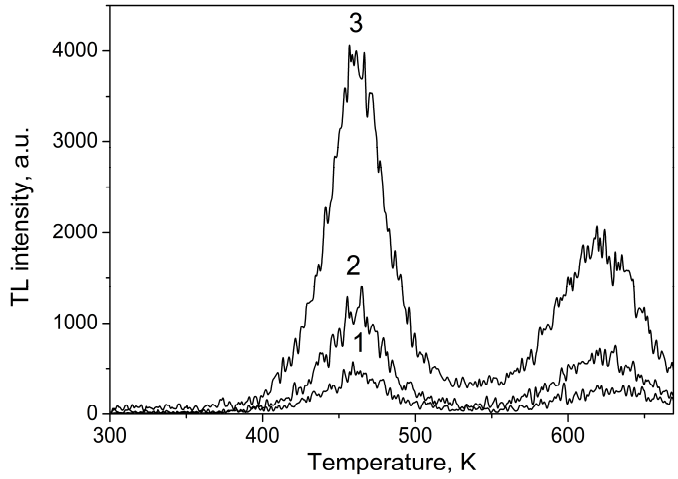

Figure 7. TL curves of alumina ceramics with manganese 1 wt. % synthesized for 2 hours (1500 °C) exposed to different doses of β-radiation: 1 – 52 Gy, 2 – 164 Gy, 3 – 987 Gy.

Figure 8 shows dose dependence of TL in the 460 K and 620 K peak of alumina ceramics. Sublinear increase in TL intensity with a growing dose is observed in the range of 3-1000 Gy for both peak. Moreover, the dose response does not have saturation even with the use of ionizing radiation close to 1 keV. It is possibly that this linear range of dose response can be broadened to higher values using more powerful sources of radiation. The maximum dose in the linear region for a low–temperature peak of 410 K did not exceed 300 Gy [15] in pure ceramics sintered at temperature of 1700°C which provides the highest radiation resistance. The linear range of dose response for such ceramics did not exceed three orders of magnitude. Using ceramics with manganese enables doses more than a one orders of magnitude higher to be registered than pure ceramics.

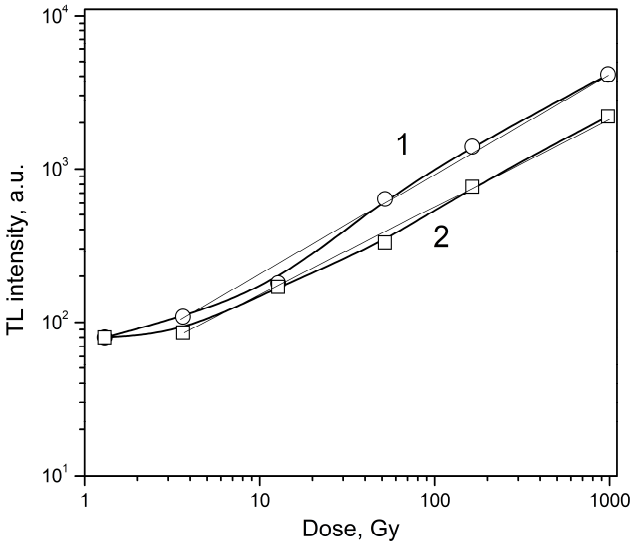

Figure 8. Dose response of the TL peak at 460 K (1) and 620 K (2) of the α-Al_2O_3:Mn ceramics annealed at 1500°C for 1 h.

4. Conclusion

In this work alumina ceramics with manganese concentration varying in a wide range are synthesized during high-temperature sintering in vacuum at various temperatures. The luminescent properties of the obtained samples were studied by the methods of PCL and TL after β-irradiation and pulse electron beam in the medium and high dose region. Quantitative data are obtained on the effect of synthesis parameters of ceramics and the concentration of manganese on PCL spectra and TL curves. It is shown that an increase in the concentration of manganese leads to quenching of the main luminescence band of internal centers of alumina ceramics as well as to the shift of the TL peaks to the high-temperature region. Al_2O_3:Mn ceramics as well as pure ceramics are sensitive to β-radiation and pulse electron irradiation. At the same time, the ceramics under study have a lower sensitivity in the main dosimetric peak compared to pure ceramics, but a higher limiting value of registered doses and an extended linear range of ionizing radiation doses. This fact can provide its prospective application for medium and high dose registration using ceramics as an ionizing radiation detector.

Acknowledgments

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